

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Kumar et al.

Applic No.: 09/085,514

Filed : May 27, 1998

For : SILICON OXIDE PARTICLES

Docket No.: 2950.02US01

Group Art Unit: 1773

Examiner: K. Bernatz

DECLARATION UNDER 37 C.F.R. § 1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

I, Rajiv K. Singh, Ph.D., hereby declare as follows:

1. I am presently a Professor of Material Science and Engineering at the University of Florida at Gainesville. Apart from my academic responsibilities, I provide consulting services through R. K. Singh Consulting Inc.
2. I received my Ph.D. degree in 1989 in Material Science and Engineering from North Carolina State University, Raleigh, NC.
3. I have been on the faculty at the University of Florida since 1990. I was promoted to Associate Professor with tenure in 1995 and to full Professor in 1997. A copy of my Curriculum Vitae is attached.
4. My recent accomplishments include receiving a National Science Foundation Young Investigator Award in 1994 and the Hardy Gold Metal for Outstanding Contributions in Material Science in

A743

-2-

1995. I was a Distinguished Visiting Professor/Scientist at National University of Singapore (1999) and National Institute for Materials and Chemical Research, Tsukuba, Japan (2000). I am a fellow of the American Society for Materials (ASM). I am the author or co-author of more than 300 scientific articles and conference proceedings. I have co-edited seven books and guest edited five journal issues.

5. I have organized over 15 international conferences in advanced processing of materials including nano-particle science and technology and chemical-mechanical polishing (CMP).

6. I have been the Associate Director of the Engineering Research Center for Particle Science and Technology, at the University of Florida from 1994 -2001. My prime responsibility at this position was to develop advanced techniques for characterization of particles.

7. I am under a Consulting Agreement with NanoGram Corporation to provide consulting services in the area of chemical-mechanical planarization. I am not a shareholder in NanoGram Corporation. Also, I have no interest in the present patent application.

8. I have been working in the area of surface polishing and material science relating to properties of inorganic particles for many years. My laboratory at the University of Florida has performed extensive experiments in particle properties and in surface polishing.

9. I have read carefully U.S. Patent 5,128,081 to Rostoker, U.S. Patent 5,128,281 to Siegel et al., U.S. Patent 5,846,310 to Noguchi et al., U.S. Patent 4,775,520 to Unger et

A744

-3-

al., and a passage from Ullmann's Encyclopedia of Industrial Chemistry, Vol. A23 at pp. 635-639. In addition, I have read the pending claims of the above noted patent application entitled "SILICON OXIDE PARTICLES." I did not participate in any capacity with the preparation of the SILICON OXIDE PARTICLES patent application.

10. With respect to the Rostoker '081 patent, a theoretical type of distribution is described in the patent. This distribution as described by Rostoker has several internal inconsistencies, as described below. Additionally, this distribution described by Rostoker does not conform to any standard representation of distribution functions described in standard textbooks and standard references.

In the Rostoker distribution, X is the average particle size. Y relates to a range around X . However, Q is important since Q , in principle, defines the size distribution. Unfortunately, the discussion of Q is not internally consistent. Q is indicated in the patent to be a dimensionless quantity. Q is defined as the concentration of particles at " X " divided by a concentration of particles in a range 3dB lower than " X ". The numerator of this expression has units of $\#/cm^3$, whereas the denominator term denoted by concentration of particles in a range of sizes 3dB below X has units of $\#/cm^2$. Thus, according to Rostoker's definition, Q is not dimensionless but has units of $1/cm$ or $1/length$. For Q to be a dimensionless quantity, either both the quantities should be defined in a certain range (e.g., concentration range +1dB of X divided by concentration at range +1dB at $X/2$), or both the quantities should describe the concentration at specific values (e.g., at X and at 3dB below X).

Even if we assume that the patent described Q as ratios at concentrations at X and at 3dB below X (which is not the case

A745

-4-

in the patent description), which makes Q dimensionless, there are several more inconsistencies. First, the particle size distribution is defined by only two points, which can be extrapolated into any distribution one might choose to elect. Secondly, if we define A as the point at which the concentration of particles in a range 3σ below x , then the concentration at A equals concentration at $X/10^{0.9}$. Then the concentration at A corresponds approximately to the concentration at X divided by 2. This value does not correspond to a Gaussian distribution, and the evaluation of A does not address the problems with the definition of Q . The Rostoker patent nowhere describes a 3 sigma (standard deviation) distribution. Also, the standard deviation cannot be defined for a distribution given in the patent.

It should be noted that the particle size distribution, as described in the Rostoker patent is not consistent with the particle size distributions that are frequently used in the standard particle size and technology books and publications. Examples of some of the standard book publications with which I am familiar are 1) A. Jilaventesa, S. Dapkunas and L.H. Lum, "Particle Size Characterization," NIST Recommended Practice Guide, NIST Special Publication, 960-1 (2001); 2) T. Allen, "Particle Size Measurement," 4th Edition, Chapman and Hall, London (1992); 3) B. H. Kaye and R. Trottier, Chemical Engineering, 99:84 (April 1995); 4) R. J. Hunter, "Foundations of Colloidal Science," Wiley (1998); 5) E. Kissa, "Dispersions, Characterization Testing and Measurement," and 6) B. V. Miller and R. Lines, CRC Critical Reviews in Analytical Chemistry, 20:75-116 (1988). Relevant pages from Reference 4 are attached.

The only source of powders described in the Rostoker '081 patent is the process described in the Siegel patent. However, the Siegel patent only describes the formation of nanocrystalline materials. In other words, the materials are polycrystalline materials with nanocrystalline domains. The

A746

-5-

Siegel patent does NOT describe the formation of submicron particles. Furthermore, I am aware of no approaches for the formation of silica particles as claimed by NanoGram except for the NanoGram process, as described further below.

11. With respect to the Unger '520 patent, this patent describes the formation of a silica gel using a two-step process.

I have considerable experience with reactions that form silica gels including the Stober process and processes similar to the Unger process, from work that has been performed in my lab in Gainesville. Also, the process that leads to the formation of silica particles from alkoxide precursors is well documented in the literature, such as the texts Sol Gel Science, by C. Jeffrey Brinker and G. Scherer, Academic Press (1990) and The Chemistry of Silica, by R. K. Iler, Wiley (1979). The first step in the Unger process uses the Stober process to form a silica gel.

In the second step, increasing the particle size and removal of the porosity further refines the sol. In both the Stober and Unger processes, the hydrolysis of the alkoxide precursors occurs in basic conditions leading to formation of sol as a result of hydrolysis, polymerization and condensation reactions. The sol particle in this process typically consists of partially coalesced small clusters that form porous structures. The clusters typically are made of trimers and tetramers of silicon-hydrogen-oxygen precursors such as $\text{SiO}(\text{OH})_3$, $\text{SiO}_2(\text{OH})_2$, $\text{Si}_4\text{O}_6(\text{OH})_6$, $\text{Si}_4\text{O}_8(\text{OH})_4$, etc. After the condensation process, the clusters contain a large number of silanol groups and siloxane bonds. Several workers have made extensive studies on the use of FTIR, NMR and Raman Spectroscopy to understand the formation of the particles. Articles by Lippert et al. and Zerda et. al. are attached.

The cluster-like aggregates making the sol particles are typically smaller than 50 nm, and have a high surface area due to formation of the porous structures. Because of the high

A747

-6-

porosity the surface area of the sols are much larger than the theoretical calculated surface area. The Unger patent also shows that the surface area of the sols of 100 - 350 m²/gm, which is typically nearly two orders of magnitude greater the theoretically calculated surface areas based on the size of the particle measured by standard techniques such as TEM, and light diffraction measurements. Thus the sols are chemically and structurally different from a non-porous silica particle which is typically obtained from the Nanogram process. Specifically, the sols may have significant chemical variation than silicon dioxides, and the aggregates do not have the uniformity described in the NanoGram claims.

12. With respect to the Noguchi patent, this patent describes the application of a coating onto the silica gel of the Unger patent. The Noguchi patent does not deal with the synthesis of silica particles.

13. Pyrolytic or flame produced process is a standard method to make small particles of silica, alumina, titania, etc. There are several references that show the details on the flame-produced process. Examples include 1) Ulmann's encyclopedia; 2) Ulrich, Combustion Science Tech. 4:47-57 (1971); 3) G. W. Scherer in Better Ceramics Through Chemistry, eds. C. J. Brinker et al. (North Holland, NY 1984); 4) D. W. Schaefer, Material Research Society Bulletin, 13:22-27 (1988); 5) J.E. Martin et al., Phys. Rev. A 33:3540-3543 (1986); 6) A. J. Hurd et al., Phys. Rev. A 35:2361-2364 (1987); 7) J. D. F. Ramsay, Colloidal Surfaces 18:207-221 (1986). Copies of References 2, 5 and 6 are attached for reference. In the flame oxidation process, the small particles, which are formed by the oxidation reaction initially aggregate with each other by a ballistic process which mean that the mean free path of the aggregating species is large, compared

A748

-7-

to the cluster size. In the second phase of the growth process, once the particles are large compared to the mean free path the trajectories of the particles change from ballistic to Brownian motion. The meandering path of the Brownian motion encourages attachment of the incoming cluster to the target periphery reacting aggregates and ramified fractal structures. Standard techniques such as visible light scattering and small angle neutron scattering have been used to show that the fractal dimension of the particles is characteristic of the diffusion limited cluster aggregation. Depending on the residence time and reactor design, the size of the primary particles may vary from 20 nm to 200 nm.

Although the primary particle size of the pyrolytic silica can be small, the particles form hard aggregates that neck in the aggregates, which make them difficult to disperse. The neck formation has been determined from transmission electron micrography (TEM). Attempts to disperse these particles result in dispersion of clusters of the fused aggregates forming individual particles. There is no way to separate the fused aggregates because the fusing results in hard bonding. Workers in field unfortunately refer to the grains that are fused together as primary particles, even though the hard fusing of these grains prevents separation of the grains as distinct particles. The actual particles are the fused entities or cluster rather than the individual 'grains'. Thus, the particles are very non-uniform even if they are formed from fused grains that may be relatively uniform.

As further support for observations from my direct experience, I have attached a TEM micrograph from my lab that provide documentary evidence of these materials formed by the process described in Ullmann's Encyclopedia. The particle have an average particle size of about 20 - 50 nm and cluster sizes on average of about 250 nm. Due to the hard fusing of these

A749

-8-

particles, the aggregates do not have high uniformity.

14. In my experiences, I have not seen materials comparable to the materials claimed in the NanoGram patent application. Based on my extensive experience with surface polishing, I expect that the NanoGram materials will be very good materials for surface polishing since the performance is expected to depend on the uniformity of the polishing materials. Thus, the NanoGram silica particles fill a void in the types of materials available for surface polishing. While NanoGram has not commercially exploited their silica materials for surface polishing yet due to their efforts with other commercial activities, I expect that these materials will someday have a significant commercial role in improving surface polishing of substrates.

14. I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date:

Dec. 10 '01

By:

Rajiv K. Singh

Rajiv K. Singh, Ph.D.

CERTIFICATE OF EXPRESS MAIL

"Express Mail" mailing label number EV 011652515 US. Date of Deposit: December 12, 2001. I hereby certify that this paper is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Box AF, Washington, DC 20231.

Glenda Anderson

Name of Person Making Deposit

Glenda Anderson

Signature

A750

Rajiv Singh

Summary of Accomplishments

- **Research Experience, Positions held and Awards**
- **Management & Leadership**
- **Research, Education & Outreach**
- **Overview of Research Programs**
- **Research Accomplishments & Milestones**
- **Selected Publications**

A751

Summary

Rajiv Singh

RAJIV K. SINGH

Materials Science and Engineering
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Research Interests and Experience

Innovative processing of materials; Chemical Mechanical Planarization (CMP); Semiconductor Integration; Laser processing; Oxide thin films; Transient thermal phenomena; Superconducting and dielectric (low K and high K) thin films; Flat-Panel Displays and Phosphors; Nano Medical Devices; Diamond and related materials; Rapid thermal processing of elemental and wide band gap semiconductors; Nano particles and Particulate coatings; Modeling of transient thermal processing; Angstrom scale advanced materials characterization, Gallium nitride and diamond crystal growth, Front and back end semiconductor cleaning, Thin film batteries; Sustained Drug Release Systems; BioMEMS;

Education

Ph.D. Materials Science and Engineering, North Carolina State University, Raleigh, 1989
M.S. Materials Science and Engineering, North Carolina State University, Raleigh, 1987
B.S. Chemical Engineering, Jadavpur University, Calcutta, India, 1985

Academic Positions

97-pre Professor, Materials Sci. and Engr., University of Florida, Gainesville, Florida
95-96 Associate Professor, Materials Sci. and Engr., University of Florida, Gainesville, Florida
90-94 Assistant Professor, Materials Sci. and Engr., University of Florida, Gainesville, Florida
89-90 Research Assistant Professor, Materials Sci. and Engr., North Carolina State University, Raleigh, North Carolina

Administrative Positions

96-pre Group Leader, Chemical Mechanical Planarization (CMP), ERC Univ. of Florida
94-01 Group Leader, Engineered Particulates, ERC, University of Florida
94-01 Associate Director, Engineering Research Center (ERC) for Particle Science & Technology

Awards/Honors

2003 *Visiting Endowed Chair Professor*, University of Texas (Austin)
2001 *Fellow: ASM* (American Society of Materials)
2000 *Visiting Professor, EPFL*, Lausanne, Switzerland
2000 *Distinguished Visiting Scientist*, NIMC, Tsukuba, Japan
2000 *University of Florida Research Foundation Award*
1999 *Distinguished Visiting Professor*, National University of Singapore, Singapore
1995 *Hardy Gold Medal* from TMS/AIME for Outstanding Contributions in Materials Science
1994 *NSF Young Investigator Award*
94-97 *Visiting Fellow*, Center for Ultrafast Optical Science (CUOS), University of Michigan
1992 *Martin Marietta Innovative Research Award*
1991 *IBM Faculty Development Award*
1989 *MRS Best Graduate Student Award*
1985 *Alumni Gold Medal* for Best Overall Graduating Senior from the University
1985 *Laha Silver Medal* for Best Graduate from College of Engineering

A752

Summary

Rajiv Singh

Management and Leadership

Research leadership: Unique and diverse research background with demonstrated excellence in several areas spanning from electronic materials, ceramics, metals, polymers to pharmaceuticals. Helped in establishing the \$66 million ERC Center for Particle Science and Technology at the University of Florida. Developed new cross disciplinary multidisciplinary programs in the university including nano-particle science and technology, chemical mechanical polishing, diamond thin films, angstrom scale characterization, particle coatings, oxide thin films, controlled drug delivery systems. Directed multidisciplinary research groups in the area of chemical mechanical polishing (CMP) and particle coatings; developing efforts in the area nano-bio technology.

Students & Educational: Graduated 21 Ph.Ds students in the last 6 years. 6 more Ph.D students expected by end of 2003. Averaging over 3 Ph.D/ year (top 1% in College of Engineering and ten times the COE average). Managing a group of over 15-20 graduate students and post doctoral researchers for the last 10 ten years. Graduate students have obtained jobs at leading academic institutions (University of Virginia, etc) and industrial institutions (Intel , Motorola, Samsung, etc.). Actively worked with minority student including recruitment and research training.

Infrastructure Development: Established the Characterization, Research Instrumentation and Test-Bed Facility (CRIT) facility for Particle Science and Technology, considered the best facility of its kind in the country. Also obtained NSF and matching funding (\$ 3 M) to acquire new state of the art microscopes (STEM-Z and FESEM) and X-ray Diffraction capabilities, which makes MAIC (Major Analytical and Instrumentation Center), one of the premier facilities of its type in the country. Set-up state of art CMP facility, laser and lamp processing lab, plasma CVD, electrical, magnetic and optical characterization facility as a part of group research efforts.

Management Leadership: Helped develop the strategic, research and administration plan for the ERC Center. Duties include, developing budgets, and managing staff members associated with the CRIT facility. Developing research plans for multidisciplinary teams on CMP, Engineered particulates and Nanoparticle Science and Technology.

International Conferences: Organized 20 international conferences (ECS, MRS, European MRS, TMS, ASM, Engineering Foundation, IUMRS (Japan), Electrochemical Society) in the area of innovative processing of materials, including nanotechnology, chemical mechanical polishing of semiconductors, laser and ion beam processing of materials, rapid thermal processing.

Industrial Interactions: Extensive interactions and joint project development with industrial partners such as Dupont, Motorola, Dow Chemical, Lucent, Applied Materials, Motorola, 3M, Intel, IBM, Ashland Chemical, Advanced Micro Devices, Westinghouse (Northrop Grumman), Seagate, etc.

Short Courses: Taught 8 short courses in the last 5 years in the area of thin films, CMP, particle coatings and nanoparticle technology, laser processing of materials at international conferences and at University of Florida.

Collaborations: Established a extensive and educational collaboration network leading to joint publications with more than 20 faculty members in the department, college of Engineering and the University. Developed a extensive collaborative research and educational network with the following institutions: University of Michigan, North Carolina State University, NC A&T State University, Southern University, EPFL (Lausanne), NUS (Singapore), NIMC (Japan), Keio University (Japan), Hiedelberg (Germany), Darmstadt (Germany), Oak Ridge National Labs, Sandia National Labs., Unicamp (Sao Paulo), CNRS Strasbourg (France), IIT Kanpur (India)

Guest Editorships: Guest editor of the October MRS Bulletin 2002 Issue on Chemical Mechanical Polishing (CMP); also guest editor of 5 other journal issues in Materials Science and Engineering B, and Journal of Electronic Materials.

Technology Licensing and Spin off: Worked with the office of licensing and technology (OTL at UF) to develop and license several technologies including cleaning of semiconductors, sustained pulmonary based drug delivery systems, slurries for chemical mechanical polishing of copper/ shallow trench isolation(STI);. Spun-off two companies including Nanotherapeutics Inc (sustained drug delivery systems) and Sinmat Inc (CMP slurries).

A753

Summary

Rajiv Singh

Research, Educational and Outreach Accomplishments: Productivity and Quality

Extensive Multidisciplinary Research Background: Research activities in the last decade spanning all broad areas of materials science including electronic materials, ceramics, metals, polymers, and bio-materials. Specific areas include silicon based electronics, wide band gap semiconductors, nano-technology, sustained drug delivery, particle coatings and thin films, nano-patterning and lithography, etc.

Publications: Over 360 refereed publications including over principal author 200 journal papers; Archival publications in Science, Physical Review B, and Applied Phys. Lett. Over 50 papers in Applied Physics Letters (the highest cited journal in electronic materials). Published more than 10 journal articles in JECS/ESST in the last 5 years. Group averaging 25 journal publications/year in the last 5 years. Publication rate among top 1 % of all MSE and engineering researchers.

Research Citations: Total citations over 2500. Average number of citations/yr >200 in the last 10 years. 5 publications with over 100 citations each. Citations of research papers within the top 1% of all materials science and engineering researchers across the globe and at the University of Florida.

Books and Book Chapters: Edited 7 books in various areas of materials processing, written 11 book chapters and review articles and appointed guest editor for 5 journals issues. Presently writing 2 textbooks in the area of CMP (30% complete) and materials characterization techniques (20% complete).

Patents: Total of 15 awarded or applied with the US Patent office. Over 50 patent disclosures with the University. [Represent the highest numbers in the college of Engineering and the University and nearly 10 times the COE average]. 5 patent filed for world-wide rights.

Invited and Contributed Talks: Presented over 130 invited talks and guest lectures. Research group has presented over 350 papers in the last 10 years at international conferences.

Softwares: Written 3 user friendly softwares, including SLIM (Simulation of Laser Interactions with Materials) which is the most widely used software in the area of laser-solid interactions. Has been used by more than 50 institutions across the globe.

Research Funding: Attracted over US \$2 million/yr in 00-01 and over \$11 million in the last 10 years. One of the key persons for the establishment of the \$66 million ERC Center for Particle Science and Technology. Also attracted substantial funding from industry (IBM, Motorola, Lockheed Martin, Sun, Ashland Chemicals, etc.). Industrial funding represents 25 % of the total award in the last 5 years.

Awards/Honors: Awarded several internationally recognized honors and awards including the Hardy Gold Medal from TMS/AIME for outstanding research contributions, ASM Fellow Award, NSF Young Investigator Award (NYI), University of Florida research foundation award. Research work featured in CNN, NY Times, Wall Street Journal and London Telegraph. Became one of the youngest full professors at the University of Florida at age 33.

Distinguished Appointments: Distinguished Visiting Professor at National University of Singapore, Distinguished Visiting scientist at NIMC (Japan), Visiting Professor at EPFL (Lausanne).

Educational Grants: Obtained educational grants (PIONEER) from NSF to train minority and graduate students. Developed IGERT proposal. Worked with minority institutions including NCA&T University and Southern University and University of Puerto-Rico.

Committee and Society Memberships: The Electrochemical Society (ECS), Materials Research Society (MRS), ASM (American Society for Materials), The Materials Society (TMS), American Vacuum Society (AVS), American Association for Advancement of Science (AAAS). Member of NSF and DOE panels, Reviewer for journals including Science, Nature, Applied Physics Letters, J. Electrochemical Society, etc

A754

Summary